

# Interplay between magnetic and lattice excitations in BiFeO<sub>3</sub>

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We have performed Raman scattering investigations on the high energy magnetic excitations in a BiFeO<sub>3</sub> single crystal as a function of both temperature and laser excitation energy. A strong feature observed at 1250 cm<sup>-1</sup> in the Raman spectra has been previously assigned to two phonon overtone. We show here that its unusual frequency shift with the excitation energy and its asymmetric temperature dependent Fano lineshape reveal a strong coupling to magnetic excitations. In the same energy range, we have also identified the two-magnon excitation with a temperature dependence very similar to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hematite.

Recently, multiferroics have attracted much attention because they exhibit a strong coupling between magnetic and ferroelectric orders.<sup>1</sup> They are good candidates for controlling the magnetic properties by electric field and vice versa<sup>2</sup> making these materials promising for potential applications in spintronics and information storage. BiFeO<sub>3</sub> (BFO) is one of the most studied multiferroic due to both its strong ferroelectric polarization<sup>3,4,5</sup> and antiferromagnetic order at room temperature<sup>6,7,8</sup>. The origin of the magnetoelectric effect in BFO remains an open issue. In order to elucidate this question, investigating the interplay between lattice vibrations and magnetic excitations appears very useful because lattice distortions strongly affect the ferroelectric polarization and therefore its coupling to magnetic order.

THz spectroscopies have recently shown to be very efficient tools for probing the coupling between the lattice and magnetic excitations. Raman<sup>9,10,11</sup> and infrared measurements<sup>12,13</sup> combined with theoretical approaches<sup>14</sup> have permitted to identify most of the vibrationnal normal modes in BFO. At the same time low-frequency magneto-optical resonances in the dielectric susceptibility of multiferroic compounds have been observed<sup>15,16,17,18</sup> and recently the cycloidal magnetic modes have been optically detected in BFO<sup>19,20</sup>. However, probing magnetic excitations and in particular their coupling to the lattice is still a challenge in BFO because we are still lacking experimental evidences for the entanglement with magnetic excitation through the phonon behaviors.

Here, we present Raman measurements on BFO single crystals aiming to address the interplay between lattice and magnetic orders. Among the two-phonon overtone features previously detected at high energy (above 700 cm<sup>-1</sup>), we show that the mode located at 1250 cm<sup>-1</sup> is much more complex than a simple double vibrational mode and exhibits a strong magnetic character. Indeed we reveal that the 1250 cm<sup>-1</sup> mode depends on the laser excitation energy and exhibits an asymmetric lineshape controlled by the spin dynamic of BFO. We have also detected in the same energy range, the signature of a

two magnon mode near 1050 cm<sup>-1</sup>, its temperature-dependence is in agreement with the one observed in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hematite.

BiFeO<sub>3</sub> single crystals were grown in air using a Bi<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> flux technique.<sup>4</sup> They are typically of millimeter size. Below a high Curie temperature ( $T_c \sim 1100$  K) BFO has a rhombohedrally distorted perovskite structure with a spontaneous electrical polarization (between 50 and 100  $\mu$ C/cm<sup>2</sup> in magnitude) along the [111] direction in the pseudo-cubic configuration.<sup>4</sup> Below the Néel temperature ( $T_N \sim 640$  K)<sup>6,7</sup>, BFO exhibits a G-type antiferromagnetic order subjected to long range modulation associated with a cycloidal spiral with a period length of 62 nm<sup>8</sup>. The spiral propagation direction is along [10-1] with a spin rotation within (-12-1) plane.

Raman measurements have been performed using several laser excitation lines between 1.92 to 2.41 eV from a mixed Ar<sup>+</sup>-Kr<sup>+</sup> gas laser. The BFO crystals were mounted in vacuum (10<sup>-6</sup> mbar) on the cold finger of a liquid helium cryostat. The Raman spectra were recorded between 7 and 300 K using a triple grating spectrometer (JY-T64000) equipped with a nitrogen cooled CCD detector. The spectrometer was in subtractive configuration with a resolution of 0.5 cm<sup>-1</sup>. The Raman spectra have been obtained using unpolarized excitation light.

The assignment of the vibrationnal modes under 700 cm<sup>-1</sup> is well known.<sup>9,10,11</sup> Group theory predicts 13 Raman active phonons for the R3C symmetry of BFO:  $\Gamma = 4A_1 + 9E$ . Above 700 cm<sup>-1</sup>, one should only detect the two-phonon Raman peaks. Two-phonon Raman scattering is a second order process involving two phonons. In contrast to one-phonon scattering process there is no restriction on the phonon wavevector but the sum of the two phonon wavevectors has to be zero. If the two phonons are identical, the two-phonon Raman peak is called an overtone.

Figure 1 shows the Raman spectra in the 1000-1300 cm<sup>-1</sup> range as a function of the laser excitation energy. We focus here on the three main peaks at 1085, 1140 and 1250 cm<sup>-1</sup> (indicated by arrows in Fig. 1). The

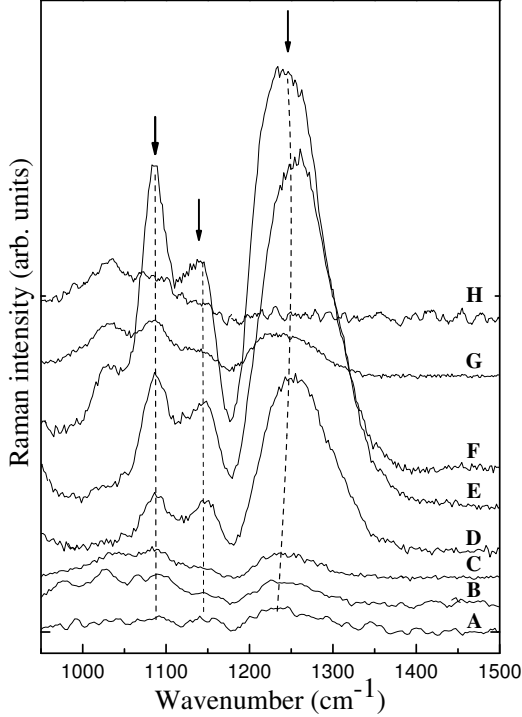


FIG. 1: Raman spectra of BiFeO<sub>3</sub> single crystal in the 900-1500 cm<sup>-1</sup> frequency range at 20K. The spectra labeled A to H were obtained from 2.71, 2.65, 2.6, 2.54, 2.41, 2.34, 2.18, 1.92 eV excitation laser lines, respectively. The Raman peaks of are indicated by arrows. Dashed lines are guides for the eyes. All spectra have been corrected for the spectral response of the spectrometer.

Raman peak intensities are strongly enhanced under the blue (2.34 eV) excitation line. These enhancements or resonance come from the matching of the incident photon energy with the absorption edge of BFO.<sup>10,21</sup> As the incident photon energy is close to the absorption edge, the probability of creating electron-hole pairs diverges and the Raman scattering efficiency is greatly enhanced.

The three peaks have been assigned to a two phonon Raman scattering process.<sup>21</sup> In particular, the prominent peak at 1250 cm<sup>-1</sup> has been previously reported by Fukumura *et al.*. Its sudden disappearance has been observed around 600 K-700 K close to  $T_N$  pointing out it's probably magnetic origin.<sup>22</sup> More recently, Ramirez *et al.* have assigned this peak to a pure two phonon process ( $2x[E_9(\text{TO}) \cong 620 \text{ cm}^{-1}]$ ).<sup>21</sup> However, the decrease of its integrated intensity up to  $T_N$  and its constant behaviour beyond  $T_N$  advocate in favor of a strong coupling between the ferroelectric and magnetic subsystems.

In Fig. 1, the two phonon modes locations at 1085 and 1140 cm<sup>-1</sup> remains constant in frequency as the excitation energy is tuned. On the contrary, the frequency of the 1250 cm<sup>-1</sup> peak increases when the excitation energy is tuned from 2.71 to 2.41 eV and then decreases. The frequency shift is about 20 cm<sup>-1</sup> as shown in Fig. 2(b).

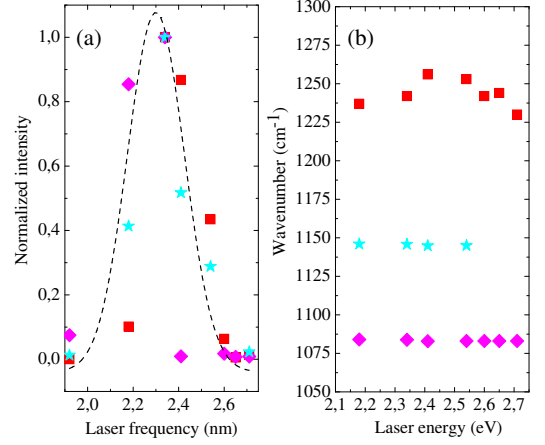


FIG. 2: (a) Intensities normalized to its maximum value and (b) wavenumber shifts as a function of the laser energy for the 1085 (diamond), 1140 (star) and 1250 cm<sup>-1</sup> (square) peaks.

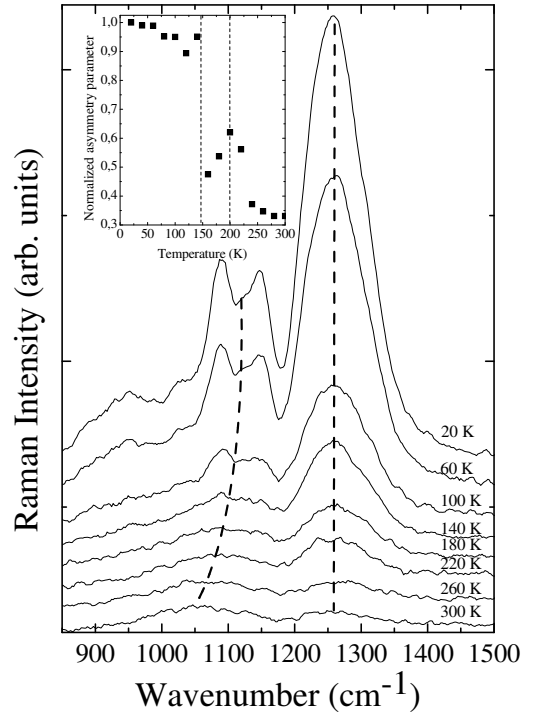


FIG. 3: Temperature dependance of the two-magnon and 1250 cm<sup>-1</sup> peaks obtained with the 2.34 eV laser line. Dashed lines are guides for the eyes. The peak at 1250 cm<sup>-1</sup> has been fitted by the Fano equation (see text). The inset shows the temperature evolution of the asymmetric parameter  $q$  corresponding to the function normalized to its maximum value.

To explain the different behaviour with the excitation energy of the 1250 cm<sup>-1</sup> overtone compare to the 1085 and 1140 cm<sup>-1</sup> one different scenarii can be put forward:

(i) The peak at 1250 cm<sup>-1</sup> is broad and might be constituted of two peaks with two different resonant behaviors with the excitation energy thus explaining the ob-

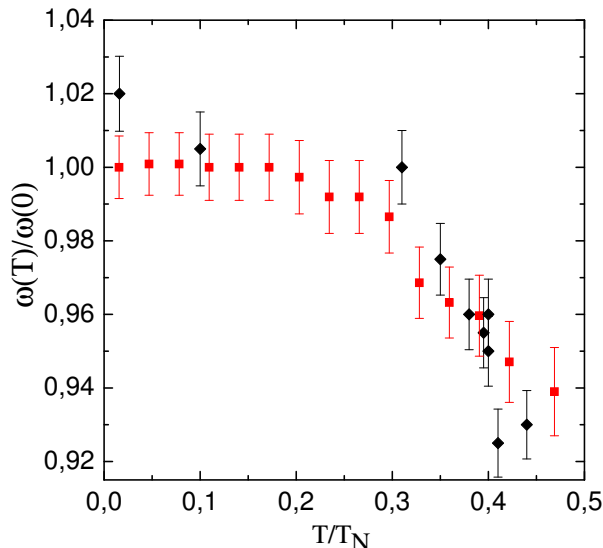


FIG. 4: **Temperature dependence** of the normalized two-magnon frequencies for BiFeO<sub>3</sub> (square) and hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (diamond).

served shift of the 1250 cm<sup>-1</sup> peak in Fig. 1. The frequency of these two peaks located at 1228 and 1288 cm<sup>-1</sup> can be deduced from a gaussian fit deconvolution of the broad 1250 cm<sup>-1</sup> peak. The 1228 and 1288 cm<sup>-1</sup> peaks should result respectively from an overtone of a peak around 615 and 645 cm<sup>-1</sup>. However, only one peak has been detected around 620 cm<sup>-1</sup> and we are led to conclude that the peak observed at 1250 cm<sup>-1</sup> is unlikely composed of two peaks.

(ii) The Raman band is associated with a luminescence process assisted by magnons or phonons. Strong exciton-phonon interactions lead to new exciton-phonon bound states which causes phonon-assisted exciton transitions. For luminescence, the transitions via the new bound states induce a continuous background which interferes with the usual discrete transitions imply in the luminescence process. This would be the origin of Fano lineshape in the phonon-assisted luminescence process. Since luminescence is produced by thermalized electron-hole pairs, the emitted photons have no correlation with the excitation lines. As a result, the frequency of the luminescence peak is independant of the excitation energy and increases monotonically with the incident photon energy. The frequency maximum of the 1250 cm<sup>-1</sup> peak in Fig. 2(b) is not consistent with this interpretation.

(iii) Such a behaviour is due to the coupling of the peak at 1250 cm<sup>-1</sup> with the antiferromagnetic order as suggested by Fukumura *et al.* and Ramirez *et al.*

In order to analyse and identify the different contributions of the three main peaks detected in the 1000-1300 cm<sup>-1</sup> range of the Raman spectra, we have performed Raman measurements as a function of tempera-

ture (from 20 to 300 K) as shown in Fig. 3. The three main peaks exhibit a small softening in energy (about 5 cm<sup>-1</sup>), gradually broaden and decrease in intensity as the temperature is raised. The peak at 1250 cm<sup>-1</sup> presents an asymmetric temperature dependent line-shape characteristic of a strong coupling between the two phonon mode and the spin excitation spectrum as we will see just below.

In order to quantify the Fano lineshape we have fitted the Raman peak located at 1250 cm<sup>-1</sup> by the Fano equation:<sup>23</sup>  $I(\omega) = I_0 \frac{(q + \frac{(\omega - \omega_0)}{\Gamma})^2}{1 + \frac{(\omega - \omega_0)^2}{\Gamma^2}}$  where  $\omega_0$  is the peak position without interaction,  $q$  is the Fano asymmetric parameter and  $\Gamma$  is the width at half maximum. The  $q$  parameter serves as a measure of the coupling between the two phonon state and a continuum of states that we have to identify.

The evolution of the normalized asymmetric parameter  $q$  as a function of the temperature is plotted in the inset of Fig. 3. A first glance on the temperature evolution of the  $q$  parameter reveals two distinct regimes:  $q(T)$  exhibits a sharp step close to  $T = 150$  K.

Recent measurements on spin waves in BFO have shown a spin-reorientation close to these two temperatures.<sup>19,20</sup> The  $q$  parameter is thus sensitive to the spin-reorientation which points out the intimate relationship between the double phonon peak at 1250 cm<sup>-1</sup> and the spin sublattice excitations. From 10 K to 150 K the asymmetric parameter  $q$  remains constant and keeps its high value indicating that the two-phonon mode is strongly coupled to the spin excitations in this temperature range. Around 150 K, the spin-phonon coupling is modified by the reorientation of the spins and sharply decreases as shown by the decrease of the  $q$  parameter. An additional feature occurs at 200 K where another spin-reorientation has been observed.<sup>20</sup> Above 200 K the asymmetry parameter decreases continuously as a mirror of the softening of the spin-phonon coupling due to thermal excitations.

In Fig. 3, the two phonons peaks at 1085 and 1140 cm<sup>-1</sup> disappear at 140 K leaving a broad and weak peak. From 140 K to 300 K this broad peak shifts from 1110 cm<sup>-1</sup> down to 1050 cm<sup>-1</sup>. The large energy softening (about 60 cm<sup>-1</sup>) of the peak with temperature is unusual compared to the one of the phonons (about 5 cm<sup>-1</sup> as mentioned before). We suspect that this large feature is related to a magnetic excitation and thus sensitive to  $T_N$ .

In order to establish the origin of this broad peak, we have studied the temperature dependence of its energy. In Fig. 4 is plotted the normalized frequency shift versus the temperature normalized to  $T_N$ . The broad peak contribution in Fig. 3 has been obtained subtracting the gaussian fit contribution of the phonon peaks. We observe softening of the frequency of the presumed two-magnon peak as a function of temperature quite consistent with the temperature dependance of the two-magnon peak previously measured in hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,

FeBO<sub>3</sub> and MnF<sub>2</sub><sup>24</sup>. For clarity, only the behaviour of the two-magnon peak in hematite has been plotted in Fig. 4. The good agreement between the two curves strongly supports the assignment of the broad peak centered at 1050 cm<sup>-1</sup> (300 K) to a two-magnon peak.

The two-magnon scattering involves two-magnons with equal and opposite wave vectors due to the momentum conservation similar to the two-phonon Raman scattering process.<sup>25</sup> The peak position related to the two-magnon scattering is expected equal to twice the zone boundary magnon energy and can be compared to the one measured in orthoferrites (RFeO<sub>3</sub> with R a rare-earth atom). In YFeO<sub>3</sub> and ErFeO<sub>3</sub> the two-magnon band is measured around 900 cm<sup>-1</sup>.<sup>26,27</sup>

We point out that the two-magnon signature should also be observed in infrared spectroscopy. In some crystal with a center of inversion the two-magnon excita-

tion through the exchange dipole moment is not allowed but can be observed using the oscillation strength of the phonon. In BFO, no inversion symmetry is found between the Fe<sup>3+</sup> ions which allow them to make significant contributions to the direct optical excitation of the two magnons.

In summary, we have tracked the magnetic excitations of the high energy Raman spectra. The complex nature of the 1250 cm<sup>-1</sup> feature have been revealed. This peak is an overtone of two phonon band with a frequency and a temperature dependance driven by its interaction with the magnetic subsystem. In addition, we have measured a weak and broad peak close to 1050 cm<sup>-1</sup> whose temperature dependence is consistent with two-magnon scattering process.

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